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DERWENT-WEEK: 200234

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TITLE: Paint base for dispersion coating used in paints and
varnishes - comprising acrylic modified fluoropolymer in
dry resin

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AMERICA INC[AQOR]

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PATENT-FAMILY:

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WO 9901505 A1	January 14, 1999	E	032	C08L 027/12
JP 2002513442 W	May 8, 2002	N/A	026	C09D 151/00
AU 9882817 A	January 25, 1999	N/A	000	C08L 027/12
EP 932645 A1	August 4, 1999	E	000	C08L 027/12
ZA 9810633 A	July 28, 1999	N/A	033	C08L 000/00
BR 9806106 A	August 31, 1999	N/A	000	C08L 027/12
NZ 335012 A	January 28, 2000	N/A	000	C09D 127/12
CN 1278285 A	December 27, 2000	N/A	000	C08L 027/12
KR 2000068392 A	November 25, 2000	N/A	000	C08L 027/12
MX 9902007 A1	June 1, 2000	N/A	000	C08L 027/12
AU 735801 B	July 12, 2001	N/A	000	C08L 027/12

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APPLICATION-DATA:

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WO 9901505A1	N/A	1998WO-US13734	July 2, 1998
JP2002513442W	N/A	1998WO-US13734	July 2, 1998
JP2002513442W	N/A	1999JP-0507356	July 2, 1998
JP2002513442W	Based on	WO 9901505	N/A
AU 9882817A	N/A	1998AU-0082817	July 2, 1998
AU 9882817A	Based on	WO 9901505	N/A
EP 932645A1	N/A	1998EP-0933065	July 2, 1998
EP 932645A1	N/A	1998WO-US13734	July 2, 1998
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ZA 9810633A	N/A	1998ZA-0010633	November 20, 1998
BR 9806106A	N/A	1998BR-0006106	July 2, 1998
BR 9806106A	N/A	1998WO-US13734	July 2, 1998
BR 9806106A	Based on	WO 9901505	N/A
NZ 335012A	N/A	1998NZ-0335012	July 2, 1998
CN 1278285A	N/A	1998CN-0800901	July 2, 1998
KR2000068392A	N/A	1998WO-US13734	July 2, 1998
KR2000068392A	N/A	1999KR-0701699	March 2, 1999
KR2000068392A	Based on	WO 9901505	N/A
MX 9902007A1	N/A	1999MX-0002007	March 1, 1999
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ABSTRACTED-PUB-NO: WO 9901505A

BASIC-ABSTRACT:

A paint base for dispersion coating comprises 10-90%wt. an acrylic modified fluoropolymer per 100%wt. of the dry resin content.

Also claimed are

(i) a coating derived by applying a paint to a surface on which a coating is desired and evaporating the thinner of the paint; and

(ii) an article having an adhered coating.

USE - Base is used for paints and varnishes for dispersion coating of substrates.

ADVANTAGE - Coatings have improved gloss, flex, crack resistance and other improved use properties e.g. solvent resistance, chemical resistance, weather resistance, heat stability, strength and resilience.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: PAINT BASE DISPERSE COATING PAINT VARNISH COMPRISE
ACRYLIC
MODIFIED DRY RESIN

DERWENT-CLASS: A14 A82 G02 P73

CPI-CODES: A04-E10; A04-F01A1; A12-B01E; A12-B01F; G02-A02C; G02-A02D;

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Polymer Index [1.1]

018 ; R00363 G0555 G0022 D01 D12 D10 D51 D53 D58 D69 D82 F* 7A ;
H0000 ; H0011*R ; S9999 S1025 S1014 ; S9999 S1489 S1478 S1456 ;
L9999 L2573 L2506 ; L9999 L2528 L2506 ; L9999 L2551 L2506 ; K9723
; P0500 F* 7A ; L9999 L2539 L2506 ; S9999 S1036 S1014

Polymer Index [1.2]

018 ; G0340*R G0339 G0260 G0022 D01 D12 D10 D26 D51 D53 D58 D63
F41 F89 G0384*R ; R00446 G0282 G0271 G0260 G0022 D01 D12 D10 D26
D51 D53 D58 D60 D83 F36 F35 ; R00460 G0306 G0271 G0260 G0022 D01
D12 D10 D26 D51 D53 D58 D60 D84 F36 F35 ; H0000 ; H0022 H0011 ;
H0033 H0011 ; L9999 L2573 L2506 ; L9999 L2528 L2506 ; L9999 L2539
L2506 ; L9999 L2551 L2506 ; S9999 S1025 S1014 ; S9999 S1490 S1478
S1456 ; S9999 S1036 S1014 ; P0088 ; P0099

Polymer Index [1.3]

018 ; H0022 H0011 ; R00363 G0555 G0022 D01 D12 D10 D51 D53 D58 D69
D82 F* 7A ; G0340*R G0339 G0260 G0022 D01 D12 D10 D26 D51 D53 D58
D63 F41 F89 G0384*R H0146 ; H0088 H0011 ; L9999 L2528 L2506 ; L9999
L2551 L2506 ; K9723 ; S9999 S1025 S1014 ; S9999 S1036 S1014 ; P0088

Polymer Index [1.4]

018 ; H0022 H0011 ; R00363 G0555 G0022 D01 D12 D10 D51 D53 D58 D69
D82 F* 7A ; R00446 G0282 G0271 G0260 G0022 D01 D12 D10 D26 D51 D53
D58 D60 D83 F36 F35 H0146 ; H0088 H0011 ; L9999 L2528 L2506 ; L9999
L2551 L2506 ; K9723 ; S9999 S1025 S1014 ; S9999 S1036 S1014 ; P0088

Polymer Index [1.5]

018 ; H0022 H0011 ; R00363 G0555 G0022 D01 D12 D10 D51 D53 D58 D69
D82 F* 7A ; R00460 G0306 G0271 G0260 G0022 D01 D12 D10 D26 D51 D53
D58 D60 D84 F36 F35 H0146 ; H0088 H0011 ; L9999 L2528 L2506 ; L9999

L2551 L2506 ; K9723 ; S9999 S1025 S1014 ; S9999 S1036 S1014 ; P0088

Polymer Index [1.6]

018 ; R00363 G0555 G0022 D01 D12 D10 D51 D53 D58 D69 D82 F* 7A ;
G0340*R G0339 G0260 G0022 D01 D12 D10 D26 D51 D53 D58 D63 F41 F89
G0384*R H0146 ; R00446 G0282 G0271 G0260 G0022 D01 D12 D10 D26 D51
D53 D58 D60 D83 F36 F35 H0146 ; R00460 G0306 G0271 G0260 G0022 D01
D12 D10 D26 D51 D53 D58 D60 D84 F36 F35 H0146 ; H0088 H0011 ; L9999
L2528 L2506 ; L9999 L2551 L2506 ; K9723 ; S9999 S1025 S1014 ; S9999
S1036 S1014 ; H0033 H0011 ; P0088

Polymer Index [1.7]

018 ; ND01 ; Q9999 Q7158*R Q7114 ; Q9999 Q7169 Q7158 Q7114 ; Q9999
Q7170 Q7158 Q7114 ; K9745*R ; K9767 K9756 K9745 ; K9778 K9745 ;
K9483*R ; K9676*R ; K9687 K9676 ; K9712 K9676 ; N9999 N7147 N7034
N7023 ; N9999 N6780*R N6655 ; B9999 B4411 B4400 B4240 ; B9999 B4035
B3930 B3838 B3747 ; B9999 B3849*R B3838 B3747 ; B9999 B4580 B4568
; B9999 B4626 B4568 ; B9999 B4682 B4568 ; B9999 B4091*R B3838 B3747
; B9999 B4024 B3963 B3930 B3838 B3747 ; N9999 N6439 ; N9999 N5947

Polymer Index [1.8]

018 ; R01966 D00 F20 Ti 4B Tr O* 6A ; A999 A102 A077

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(21) International Application Number: PCT/US98/13734 (22) International Filing Date: 2 July 1998 (02.07.98) (30) Priority Data: 60/051,642 2 July 1997 (02.07.97) US 09/108,764 1 July 1998 (01.07.98) US (71) Applicant: ELF ATOCHEM NORTH AMERICA, INC. [US/US]; 2000 Market Street, Philadelphia, PA-19103-3222 (US). (72) Inventors: GABOURY, Scott, R.; 1201 Hunter Drive, Blue Bell, PA 19422 (US). DRUJON, Xavier, F.; Domain de Perpignaa, 5, boulevard des Pyrenees, F-64110 Jurançon (FR). (74) Agents: MARCUS, Stanley, A. et al.; Elf Atochem North America, Inc., 2000 Market Street, Philadelphia, PA 19103-3222 (US).		(81) Designated States: AU, BR, CA, CN, JP, KR, MX, NZ, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: FLUOROPOLYMER DISPERSION COATINGS FROM MODIFIED THERMOPLASTIC VINYLIDENE FLUORIDE BASED RESINS		
(57) Abstract A paint base for dispersion coatings substrates comprising an acrylic modified fluoropolymer, paints and varnishes derived therefrom, coatings derived therefrom and articles coated with said coatings are disclosed. The coatings have improved gloss, flex, crack resistance and other improved use properties.		

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FLUOROPOLYMER DISPERSION COATINGS FROM MODIFIED
THERMOPLASTIC VINYLIDENE FLUORIDE BASED RESINS

IR 3501 NP

This application claims priority from U.S.
Provisional Application Serial No. 60/051,642 filed
5 July 2, 1997.

FIELD OF THE INVENTION

This invention relates to compositions of matter
classified in the art of chemistry as seed polymers
based on fluoropolymers, more specifically homo
10 polymers of vinylidene fluoride (VDF) and copolymers
of vinylidene fluoride with comonomers selected from
hexafluoropropylene (HFP) tetrafluoroethylene (TFE),
chlorotrifluoroethylene (CTFE), trifluoroethylene
(TrFE), and/or vinylfluoride (VF), in combination with
15 polymers based on acrylic acid, acrylic acid esters,
methacrylic acid and/or methacrylic acid esters
(acrylic polymers), to compositions containing them,
more specifically to liquid coating compositions

containing them, and to processes for the preparation and use of the compositions containing the seed polymers of fluoropolymers and acrylic polymers and for the use of the fluoropolymers and acrylic polymers combinations themselves.

5

BACKGROUND OF THE INVENTION

Coatings made through use of paint binders and paint vehicles formulated from polyvinylidene fluoride (PVDF) polymer resins are known to provide good solvent resistance, chemical resistance, weather resistance, heat stability, strength and resilience. However, there is a desire for further improvement, particularly in exterior durability in harsh environments. In addition, the mechanism of film formation in conventional polyvinylidene fluoride (PVDF) based dispersion coatings and the industrial conditions under which these coatings are applied lead to medium gloss coatings, typically 30 to 40 as measured with 60 degree gloss geometry. The nature of conventional PVDF dispersion paints is a mixture of discrete PVDF particles into a homogeneous acrylic solution phase or discrete PVDF particles and discrete acrylic particles in an aqueous phase. These systems may or may not contain pigments and other additives as well. It is known in the art that in order to develop optimum properties from this type of paint system, the PVDF and acrylic phases must mix during film formation. In the case of coil coating, which is one common application of this type of coatings system,

film formation times of 30 to 60 seconds are typical. Short bake cycles offer little time for complete PVDF and acrylic mixing.

It has been found that the formulation of vehicles and binders for paints and varnishes from the combinations of PVDF homo and copolymers and acrylic polymers described more fully below provides coatings with higher gloss levels than conventional prior art PVDF acrylic blended resin paint systems. In addition, the mechanical flexibility of the coatings provided by the present invention is improved over prior art blended systems under certain formulation and baking conditions. Accelerated ultraviolet light (UV) resistance testing by standard methods indicates that coatings provided by the present invention have improved UV resistance compared to prior art blended resin systems as shown by improved gloss retention.

PRIOR ART

There are numerous published patents and patent applications worldwide which describe the use of particles in a latex of polyvinylidene fluoride hom- or co-polymers as seeds for the polymerization of various acrylic monomers to form latices from which aqueous based paints and other coatings materials are formed directly without isolation of the polymers from the latices. See, for example, U.S. Patent 5,439,980, 4,946,889, 5,034,460; European Patent Applications 0 670 353 A2, 0 736 583 A1, 0 360 575 A2; Japanese Applications 6-335005 (8-170045), 4-97306 (5-271359),

3-355973 (5-170909), 3-124997 (4-325509), 7-63193 (8-259773); PCT Applications WO 95/08582, and the following abstracts - Chem. Abstr. 1994: 702216, Chem. Abstr. 1993, 474687, Derwent 93: 278324, Derwent 91: 329278, Derwent 90: 317958, Derwent 87: 082345, Derwent 86: 213626, Derwent 94: 107015/13, Derwent 93: 365288/46, Derwent 93: 365461/46, Derwent 96: 049627, Derwent 93: 397686, Derwent 94: 808169 and the references cited in these publications. None of these publications teach or suggest isolation of the solids from the seed polymerization latex and subsequent redispersion of the recovered solids in aqueous or nonaqueous solvents to form dispersion type paints and varnishes.

There are a number of patents and publications which teach dispersion type paint and varnish compositions based on polyvinylidene fluoride polymers and copolymers physically mixed with acrylic polymers. See, for example, U.S. Patent 3,324,069, U.S. Patent 4,128,519, PCT Application WO 93/13178 and European Patent Application 0 670 353 A2 and the references cited therein. Nothing in any of these references suggests the improved properties provided to paint and varnish applied coatings by the compositions of the instant invention.

DEFINITIONS

As used herein and in the appended claims, the terms "paint base" or "paint vehicle" comprehend the combination of paint binder and thinner into which

pigment is mixed to form a paint. As used herein and in the appended claims, the term "varnish" comprehends a liquid composition which is converted to a transparent solid after application as a thin layer. A paint base or paint vehicle without added pigment can be a varnish.

As used herein and in the appended claims, the terms "binder" or "paint binder" comprehend the non-volatile portion of a paint base or paint vehicle. It holds pigment particles together and the paint film as a whole to the material on which it is applied.

As used herein and in the appended claims, "thinner" comprehends the portion of paint (or varnish) which volatilizes during the drying process. It includes any solvent (aqueous or non-aqueous).

As used herein and in the appended claims, "acrylic modified fluoropolymer" ("AMF") means the solid resin (particles or agglomerated) prepared by polymerizing ethylenically unsaturated monomers selected from the group acrylic acid, acrylic acid esters, methacrylic acid, methacrylic acid esters and mixtures thereof in the presence of a latex of vinylidene fluoride homo- or copolymers as described in more detail below and isolating, if necessary, the resin from the latex resulting from its preparation.

As used herein and in the appended claims "dispersion coating" means a coating where the paint base or vehicle is made from substantially dry resin, isolated from the latex resulting from its preparation, dissolved or suspended in thinner.

Thus, a paint base for a dispersion coating will be one wherein the paint base will contain substantially only resin isolated from any latex it was initially formed in, if necessary, and substantially dried.

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SUMMARY OF THE INVENTION

The invention provides in a first composition aspect, a paint base or paint vehicle for dispersion coating which comprises in an amount of from 10% to 90% by weight of the dry resin content, an acrylic modified fluoropolymer resin.

Special mention is made of embodiments of the first composition aspect of the invention wherein the thinner for the paint base or paint vehicle is substantially non-aqueous.

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Still further special mention is made of embodiments of the first composition aspect of the invention wherein the thinner for the paint base or paint vehicle is aqueous based.

20

The invention provides in a second composition aspect a paint comprising the paint base or paint vehicle of the first composition aspect of the invention and a pigment mixed therein.

25

The invention provides in a third composition aspect, a coating derived by applying a paint as defined in the second composition aspect of the invention or a varnish consisting essentially of a paint base or paint vehicle as defined in the first composition aspect of the invention to a surface on

which a coating is desired and evaporating the solvent contained in said paint or varnish.

The invention provides in a fourth composition aspect, an article of manufacture comprising an article having adhered on at least one surface thereof a coating as defined in the third composition aspect of the invention.

The invention provides in a process aspect, a process for applying an improved acrylic modified fluoropolymer binder containing coating on a surface which comprises applying a paint as defined in the second composition aspect of the invention or a varnish consisting essentially of a paint base or paint vehicle as defined in the first composition aspect of the invention to said surface and evaporating the thinner from said paint or varnish.

DETAILED DESCRIPTION OF THE INVENTION

The invention will now generally be described with reference to preferred embodiments thereof so as to enable one of skill in the art to make and use same.

The vinylidene fluoride homo- and copolymer emulsions employed as a starting material are known, as are their methods of preparation. See, for example, Humphrey and Dohany, Vinylidene Fluoride Polymers, Encyclopedia of Polymer Science and Engineering, 2nd Edition, Vol. 17, pp. 532 to 548, 1989, John Wiley and Sons, and the references cited therein. See also U.S. Patents 3,857,827; 4,360,652;

4,569,978; 3,051,677; 3,178,399; 5,093,427; 4,076,929;
5,543,217; Moggi et al., Polymer Bulletin, 7, pp 115
to 122, (1982), Bonardelli et al., Polymer, 27, pp.
905-909 (1986), Pianca, et al., Polymer, 28, pp 224 to
230 (1987), and Abusleme et al., European Patent
5 Appln. No. 650,982 A1. The latices so prepared may be
homopolymer PVDF or copolymer PVDF with suitable
monomers for copolymerization with VDF being selected
from HFP, TFE, TrFE, VF or mixtures thereof. HFP is a
preferred comonomer.

10 Up to about 30% by weight comonomer(s) may be
incorporated in PVDF copolymers with from about 0% to
about 25% by weight being preferred.

Seed particles having Tg less than 25°C are
preferred for this invention. Techniques for
15 controlling Tg are well known in the art and are not
per se part of this invention. The most common method
of control of Tg for fluorocopolymers is by control of
the fluorocopolymer composition.

It is also preferred that the seed particle size
20 should be less than 250 nm. in order to obtain a final
AMF polymer particle size of less than 350 nm.

Use of emulsion or suspension polymerization in
vertical or horizontal reactors in batch, semi-
continuous or continuous mode is contemplated by the
25 invention.

The acrylic and methacrylic monomer that are seed
polymerized in the presence of the fluoropolymer latex
are acrylic acid, acrylic acid alkyl esters,
methacrylic acid and methacrylic acid alkyl esters

wherein the alkyl group in the ester portion of the molecule is from 1 to about 10 carbon atoms, with from 1 to about 4 carbons being preferred.

Suitable acrylic esters include, without limitation, ethylacrylate, methylacrylate, butylacrylate, propylacrylate, isobutylacrylate, amylacrylate, 2-ethylhexylacrylate, and hexylacrylate.

Suitable methacrylic acid esters include without limitation, ethyl methacrylate, methyl methacrylate, butyl methacrylate, propyl methacrylate, isobutyl methacrylate, amyl methacrylate, 2-ethylhexyl methacrylate and hydroxyethyl methacrylate. Preferred monomers are acrylic acid methacrylic acid, ethyl acrylate, methyl acrylate, butyl acrylate, methyl methacrylate and glycidyl methacrylate. The acrylate and methacrylate ester monomers may be used singly or in combination.

For fine tuning properties of the final formed paint films, small quantities of other copolymerizable monomers and/or oligomers may be copolymerized with the acrylic and/or methacrylic acid and ester monomers. These include, without limitation, acrylonitrile, conjugated dienes, such as, 1,3-butadiene and isoprene, fluoroalkyl acrylates, fluoroacrylalkyl methacrylates, aromatic alkenyl compounds, such as, styrene, α -methylstyrene, styrene halides and divinyl hydrocarbon compounds, such as, divinyl benzene. Reactive emulsifiers, such as those available under the tradenames, Burena, Eliminol, NK ester, may be used.

The total amount of acrylic acid, acrylic esters, methacrylic acid, methacrylic acid esters or mixtures thereof should be 80% or greater, preferably 90% or greater by weight of the total monomer mixture.

5 The total monomer mixture for polymerization or copolymerization in the presence of the fluoropolymer seed particles should be 10 to 200 parts by weight, preferably 20 to 80 parts by weight per 100 parts by weight of seed particles.

10 The seed polymerization can be carried out under the same conditions as for conventional emulsion polymerizations. The desired acrylic and/or methacrylic monomer(s) and a polymerization initiator and, optionally, a surfactant, a chain transfer agent, a pH regulator, and, also optionally, eventually a
15 solvent and a chelating agent, are added to the seed latex, and reaction is carried out under atmospheric pressure, 0.5 to 6 hours at temperatures of 20 to 90°C, preferably 40 to 80°C.

20 The emulsion polymerization using the fluoropolymer as a seed can be performed according to standard methods:

Batch polymerization, wherein the monomer(s), the initiator and the other ingredients, if required, are added to the aqueous fluoropolymer dispersion from the
25 beginning;

Semi-continuous polymerization, wherein a part or all of one of the ingredients is fed continuously or batch-wise during the reaction;

Continuous polymerization, wherein all the ingredients and the aqueous fluoropolymer dispersion are simultaneously fed into a reactor.

The ingredients may be added to the reactor neat, solubilized in a suitable solvent (organic or aqueous) or as a dispersion in a suitable solvent.

Use of all types of polymerization reactors (stirred tank, tubular, loop) is contemplated by the invention. A stirred tank reactor operating in the semi-continuous mode is preferred because of its convenience and flexibility.

The process used to manufacture the products of the invention involves at least two stages. At least one stage is required for the emulsion polymerization of the fluoropolymer and at least one is required for the seeded emulsion polymerization of the acrylic monomer(s).

These stages can be performed in the same reactor or different reactors. Each stage may contain its specific monomers, surfactant, initiator, chain transfer agent, pH regulator, solvent and/or chelating agents. It is preferred that the same reactor be employed for the various stages.

The final latex may be composed of dispersed particles, homogeneous in size and composition, or of dispersed particles having several populations of size and/or of composition. Latex having a homogeneous composition distribution of the dispersed particles is preferred. A broad particle size distribution, or a multi-modal particle size distribution allowing

efficient packing of the particles, may be preferred to a homogeneous particle size distribution.

The final latex particles may be composed of one, two or more phases of various morphologies such as single phase morphology, core-shell, half-moon, inverse core shell, strawberry, snow ball men, interpenetrating network and the like, all of which are well known in the art as are the techniques of obtaining same. The preferred morphologies are fluoropolymer cores/acrylic shells, latex particles and homogeneous latex particles. A single phase latex particle morphology can be obtained with miscible fluoropolymer/acrylic polymer pairs or with interpenetrating networks.

The surfactant that can be used includes anionic surfactants, cationic surfactants, non-ionic surfactants and amphoteric surfactants. They can be used separately or in combinations of two or more, with the proviso that obviously incompatible types cannot be combined. They can be mixed with the seed latex, or with the monomer mixture, or in any suitable combination with other polymerization ingredients. The anionic surfactant includes esters of higher alcohol sulfates (e.g. sodium salts of alkyl sulfonic acids, sodium salts of alkyl benzene sulfonic acids, sodium salts of succinic acids, sodium salts of succinic acid dialkyl ester sulfonic acids, sodium salts of alkyl diphenyether disulfonic acids). Suitable cationic surfactants are an alkyl pyridinium chloride or an alkylammonium chloride. The non-ionic

surfactant includes polyoxyethylene alkyl phenyl ethers, polyoxyethylene alkyl ethers, polyoxyethylene alkyl esters, polyoxyethylene alkyl phenyl esters, glycerol esters, sorbitan alkyl esters, and derivatives thereof. A suitable amphoteric surfactant is lauryl betaine. Reactive emulsifiers, which are able to copolymerize with the above-mentioned monomers, can also be used (e.g. sodium styrene sulfonate, sodium alkyl sulfonate, sodium aryl alkyl sulfonate). The amount of surfactant usually used is 0.05 to 5 parts by weight per 100 parts by weight of total fluoropolymer particles.

Any kind of initiator which produces radicals suitable for free radical polymerization in aqueous media, for temperatures from 20 to 100°C, can be used as the polymerization initiator. They can be used alone or in combination with a reducing agent (e.g. sodium hydrogenobisulfite, sodium L-ascorbate, sodium thiosulfate, sodium hydrogensulfite). For example, persulfates, hydrogen peroxide, can be used as water-soluble initiators, and cumene hydroperoxide, diisopropyl peroxy carbonate, benzoyl peroxide, 2,2'-azobis methyl butanenitrile, 2,2'-azobisisobutyronitrile, 1,1'-azobiscyclohexane-1-carbonitrile, isopropylbenzenehydroperoxyde can be used as oil-soluble initiators. Preferred initiators are 2,2'-azobis methylbutanenitrile and 1,1'-azobiscyclohexane-1-carbonitrile. The oil-soluble initiator could be dissolved in a small quantity of solvent if desired. The amount of initiator used is

0.1 to 2 parts by weight per 100 parts by weight of the monomer mixture added.

There are no limitations in the type of chain transfer agents that can be used, as long as they do not excessively slow down the reaction. The chain transfer agents that can be used include for example mercaptans (e.g. dodecyl mercaptan, octylmercaptan), halogenated hydrocarbon (e.g. carbon tetrachloride, chloroform), xanthogen (e.g. dimethylxanthogen disulfide). The quantity of chain transfer agent used is usually 0 to 5 parts by weight per 100 parts by weight of the monomer mixture added.

A small quantity of solvent can be added during the reaction in order to help swell the seed particle. The quantity of solvent added should be in such ranges that workability, environmental safety, production safety, fire hazard prevention, are not impaired.

The quantity of pH adjusting agents (e.g. sodium carbonate, potassium carbonate, sodium hydrogenocarbonate) and chelating agents (e.g. ethylene diamine tetraacetic acid, glycine, alanine) used are 0 to 2 parts by weight and 0 to 0.1 per 100 parts by weight of the monomer mixture added, respectively.

Additional amount of surfactants or pH adjusting agents can be added to the final latex. This usually helps in improving storage stability.

A further description of preferred methods of synthesis of AMF polymers and of the monomers which may be used therein is given in European Patent 0 360

575 B1 and Japanese Patent Application 4-97306.

Isolation of the acrylic modified fluoropolymer resin from the seed polymer latex may be accomplished by standard methods well known in the art such as, drying of the latex, coagulation by high shear mixing, centrifugation, and/or altering the ionic balance and/or freezing followed by filtration and optional washing and the like.

The paint base or paint vehicle composition may be left unpigmented to form a varnish, or it may be mixed with one or more pigments to form a paint. The same pigments useful in other PVDF based coatings may satisfactorily be used in the practice of the present invention. The pigments include, for example, those pigments identified in U.S. Patent No. 3,340,222. The pigment may be organic or inorganic. According to one embodiment, the pigment may comprise titanium dioxide, or titanium dioxide in combination with one or more other inorganic pigments wherein titanium dioxide comprises the major part of the combination.

Inorganic pigments which may be used alone or in combination with titanium dioxide include, for example, silica, iron oxides of various colors, cadmiums, lead titanate, and various silicates, for example, talc, diatomaceous earth, asbestos, mica, clay, and basic lead silicate. Pigments which may be used in combination with titanium dioxide include, for example, zinc oxide, zinc sulfide, zirconium oxide, white lead, carbon black, lead chromate, leafing and non-leafing metallic pigments, molybdate orange,

calcium carbonate and barium sulfate.

The preferred pigment category is the ceramic metal oxide type pigments which are calcined. Chromium oxides and some iron oxides of the calcined type may also be satisfactorily utilized. For applications where a white coating is desired, a non-chalking, non-yellowing rutile-type of titanium dioxide is recommended. Lithopones and the like are inadequate as they suffer from lack of chalk resistance and/or from inadequate hiding. Anastase TiO₂ is similarly not recommended.

The pigment component, when present, is advantageously present in the composition in the amount of from about 0.1 to about 50 parts by weight per 100 parts of resin component. While for most applications the preferred range is from about 25 to about 35 parts by weight pigment per 100 parts of resin component, for white and light colored pigment the amount of pigment is generally in the higher ranges of the preferred amount, and may be as high as 35 parts by weight per 100 parts of resin component or higher.

Clear metallic pigmented coats will have very low amounts by weight of pigment.

As paint bases or paint vehicles, the compositions of the invention will be in liquid form. The binder comprising the fluoropolymer resin and any optional other resins contained therein will be, dispersed, partially or completely dissolved in a thinner which may comprise either aqueous or non-

aqueous based solvents. Such solvents may either be single solvents or mixtures of solvents. Suitable aqueous based solvents are described in U.S. Patent 4,128,519. Suitable non-aqueous based solvents are described in WO 93/13178 and U.S. Patent 3,324,069.

5 The solvents employed are not per se part of this invention and any conventional solvent or mixture of solvents including latent solvents conventionally employed in PVDF resin based paints is contemplated as suitable by the invention.

10 Other conventional paint components, such as surfactants, dispersants, waxes, crosslinking agents, UV absorbers, flatting agents, thickeners and the like may also be included in the paint base or paint vehicle and the paint and varnish compositions of the
15 invention.

Standard techniques, well known to those of skill in the art, may be employed to mix the ingredients
~~contained in the paint base or paint vehicle and the~~
paint and varnish compositions contemplated by the
20 present invention.

The paint and varnish compositions of this invention may be applied to a wide variety of substrates including plastics, wood, metals, ceramics, glass and the like by conventional coating methods,
25 such as spraying, brushing, dipping, casting, knife coating, coil coating, reverse roll coating, draw down and other methods known in the art.

After application, solvent based paints and varnishes having the resins in solution are air-dried

to remove the thinner, including the solvent, at ambient temperatures, 15° to 50°C, and other aqueous and non-aqueous solvent based paints and varnishes are baked or heated to evaporate the thinner, including the solvent, and coalesce the coating. The heating
5 temperatures will range from about 125° to about 300°C, preferably from about 175° to about 275°C. Obviously for coating substrates sensitive to the higher temperature range, solvent based paints and varnishes having the resin totally dissolved should be employed.

10 Although adherence of the polymer film formed on drying the paint and varnish compositions to the substrate is normally more than adequate, increased adhesion may be obtained by first priming the substrate surface with a compatible coating layer.

15 For example, for wood, a useful primer is a layer of pigmented acrylic acid ester polymer as described in U.S. Patent 3,234,039 and in U.S. Patent 3,037,881.

~~For metal coatings, for aqueous based paint and~~
varnish compositions, a preferred primer layer is
20 described in U.S. Patent 3,111,426 that is an epoxy based primer. More generally, acrylic based primers such as described in U.S. Patent 3,526,532 and the primers of U.S. Patent 4,179,542 based on mixtures of partially fluorinated halogenated ethylene polymers,
25 epoxy resins, powdered metallic pigments and wet ground mica are also useful on metals. For coatings on glass, as well as glass cloth, glass fibers or other flexible substrates, woven or non-woven, known adhesion promoters may be used. In particular, glass

fiber may first be treated with a silane coupling agent as described by I.L. Fan and R. G. Shaw, Rubber World, June 1971, page 56.

Air drying of the solvent based paints and varnishes of the invention having the resins in solution on substrates such as paper, glass fiber, glass cloth, and non-woven textiles may be accomplished at ambient temperatures with drying periods of from about 3 to 24 hours. However, with forced air drying at about 50°C the films will dry in 10 to 15 minutes. At 60°C about 5 to 10 minutes are adequate using forced air drying. After application, other aqueous and non-aqueous based systems are subjected to heat to evaporate the thinner, including the solvent, and subject the polymers to coalescence. As stated above, the heating temperatures will range from about 125°C to about 300°C, preferably between about 175°C and 275° and most preferably between about 215°C and 250°C.

Alternatively, the paints and varnishes of the invention may be cast and subjected to heating to obtain a free film of the composition. In all cases, coatings are smooth, glossy, uniform and adhere tenaciously to the substrate. The films and coatings are also hard, creep resistant (that is dimensionally stable), flexible, chemically resistant and weather resistant. Smoke generation resistance and hydrophobicity are also provided by the films and coatings.

The following examples further illustrate the best mode contemplated by the inventors for the practice of their invention and should be considered

as illustrative and not in limitation thereof.

The following examples demonstrate that AMF resins provide coatings with higher gloss levels than conventional PVDF/acrylic blended paint systems. In addition, the flexibility of the AMF coatings are improved over blended systems under certain formulation and baking conditions. Accelerated UV testing indicates that the AMF based coatings having improved UV resistance as shown by improved gloss retention as compared to blended systems.

Example 1: White coatings at 70/30 PVDF/acrylic ratio

Formulations A, B, and C were prepared containing components outlined in Table I. For each formulation, the components were charged into a grinding container and 4 mm glass beads were added to each formulation in the amount of 1.25 times the total formulation weight. The paint formulations were milled for one hour. The base resin used in formulation A was an AMF containing a PVDF to acrylic weight ratio of 80/20, and formulations B and C used two different PVDF homopolymers. Secondary acrylic resin was added to each formulation such that all formulations were at a final fluoropolymer to acrylic weight ratio of 70/30. Note that toluene was added only to formulation A to account for toluene added into formulations B and C with the Acryloid B-44S.

Table I

	Weight Percent of Formulation Components		
	Formulation A	Formulation B	Formulation C
Base Resin	25.6 (AMF1@PVDF/ Acrylic=80/20)	20.5 (PVDF 1)	20.5 (PVDF 2)
Ti-Pure R-960**	15.8	15.8	15.8
Acryloid B-44S* (40% solids in toluene)	9.1	21.9	21.9
Toluene	47.7	47.7	47.7
Isophorone	41.8	41.8	41.8
Total Fluoropolymer/ Acrylic Ratio	70/30	70/30	70/30

*Copolymer of methyl methacrylate and ethyl acrylate (Rohm and Haas Co., Phila., PA).

**Ti-Pure is a registered trademark of DuPont for their titanium dioxide grades.

A wire drawdown applicator was used to apply each paint to aluminum panels, and the coated panels were baked at 525°F for 90 seconds. After baking, panels were post treated either by immediate immersion in room temperature water, quenched, or a secondary bake at 140°C for 24 hours, annealed. Table II shows gloss and flexibility test results for these panels. AMF formulation A has a higher gloss than both PVDF formulations B and C when quenched or annealed. Also, the high flexibility of the quenched coatings is maintained only by formulation A. Formulations B and C both lose some degree of flexibility upon annealing. Surface SEM photos of quenched coatings prepared from formulations A and C were examined. The SEM photos clearly show that the AMF coating has a

significantly smoother surface than the PVDF/acrylic blended coating. This is also in agreement with the higher gloss of the AMF coating.

Table II

	Coating Properties		
	Formulation A	Formulation B	Formulation C
60 Degree Gloss of Quenched Coating	68	41	45
60 Degree Gloss of Annealed Coating	42	37	35
T-Bend Flexibility of Quenched Coating	0-T	0-T	0-T
T-Bend Flexibility of Annealed Coating	0-T	4-T	2-T

Example 2: White coatings at 80/20 PVDF/acrylic ratio

Formulations D and E were prepared containing components outlined in Table III. For each

formulation, the components were charged into a grinding container and 4 mm glass beads were added to each formulation in the amount of 1.25 times the total formulation weight. The paint formulations were milled for one hour. The base resin used in formulation D was an AMF containing a PVDF to acrylic weight ratio of 80/20, and formulation E base resin was PVDF homopolymer. Secondary acrylic resin was added to formulation E such that both formulations were at a final fluoropolymer to acrylic weight ratio of 80/20. Note that toluene was added into formulation D only to account for toluene added into

formulation E in the Acryloid B-44S.

Table III

	Weight Percent of Component	
	Formulation D	Formulation E
Resin	29.2 (AMF1@PVDF/ Acrylic=80/20)	23.4 (PVDF 2)
Ti-Pure R-960	15.8	15.8
Acryloid B-44S (40% solids in toluene)	--	14.6
Toluene	8.8	--
Isophorone	46.2	46.2
Total Fluoropolymer/Acrylic Ratio	80/20	80/20

A wire wound drawdown applicator was used to apply each paint to aluminum panels, and the coated panels were baked at 525°F for 90 seconds. After baking, panels were post treated either by immediate immersion in room temperature water, quenched, or a secondary bake at 140°C for 24 hours, annealed. Table IV shows gloss and flexibility test results for these panels. AMF formulation D has a higher gloss than PVDF formulation E when quenched or annealed. In this case, the high flexibility of the coatings is maintained for both formulations under both post treatment conditions.

Table IV

	Coating Properties	
	Formulation D	Formulation E
60 Degree Gloss of Quenched Coating	68	34
60 Degree Gloss of Annealed Coating	47	28
T-Bend Flexibility of Quenched Coating	0-T	0-T
T-Bend Flexibility of Annealed Coating	0-T	0-T

Example 3

- 10 Formulations F and G were prepared containing components outlined in Table V. For each formulation, the components were charged into a grinding container and 4 mm glass beads were added to each formulation in the amount of 1.25 times the total formulation weight.
- 15 The paint formulations were milled for one hour. The base resin used in formulation F was an AMF containing PVDF to acrylic weight ratio of 70/30, and formulation G base resin was PVDF homopolymer. Secondary acrylic resin was added to formulation G such that both
- 20 formulations were at a final fluoropolymer to acrylic weight ratio of 70/30.

Table V

	Weight Percent of Component	
	Formulation F	Formulation G
Resin	29.2 (AMF2@PVDF/ Acrylic=70/30)	20.5 (PVDF 3)
Ti-Pure R-960	15.8	15.8
Acryloid B-44S (40% solids in toluene)	--	21.9
Isophorone	55.0	41.8
Total Fluoropolymer/Acrylic Ratio	70/30	70/30
Original 60 Degree Gloss - Quenched	56	36
60 Degree Gloss of Coating after 15,000 hours of QUV-B Exposure	58	22
Percent Gloss Retention of Coating after 15,000 hours of QUV-B Exposure	104	61

A wire wound drawdown applicator was used to apply each paint to aluminum panels, and the coated panels were baked at 550°F for 90 seconds and immediately quenched into room temperature water. As shown in Table V, AMF formulation F gives a higher original gloss than PVDF formulation G. After 15,000 hours of fluorescent UV-B exposure, the AMF coating also maintains a higher percentage of the original gloss.

Example 4: Water Based Dispersion Coating of VDF-HFP based AMF

A 100 g paint batch was prepared from Formulation

H by charging components 1 to 6, in the ratios shown in Table VI, into a grinding container with 100 g of 4 mm glass milling beads. The mixture was milled for 2 hours and strained through a coarse filter to remove the milling media. Component 7 and 8 were added to the strained mixture, and the mixture was rolled slowly for approximately 2 hours. The paint was applied to aluminum panels with a wire wound drawdown applicator chosen to produce 20-25 micron dry coatings. Coated panels baked at 450°F for 10 minutes produced smooth continuous coatings. The coatings passed 0-T flexibility testing, 100% crosshatch adhesion, and 60 inch-pounds (the maximum load which does not produce substrate rupture) of direct or reverse impact without cracking.

Table VI: Formulation H

Components	Weight Percent
1) AMF Resin	44.0 (VDF-HFP/Acrylic=62-8/30)
2) Deionized Water	44.0
3) Dipropylene glycol	3.5
4) Tripropylene glycol methyl ether	3.5
5) Ethylene glycol butyl ether	1.0
6) Rhone-Poulenc Colloid® 643*	0.5
7) N-methyl pyrrolidinone	3.5
8) Dimethyl amino ethanol	amount needed to adjust pH to 8-9

*= Proprietary Defoamer

T-Bend formability was determined according to ASTM D 4145-83 (Reapproved 1990) a Standard Test

Method for Coating Flexibility of Prepainted Sheet.

In this test, prepainted coated panels are bent 180° around progressively more thicknesses of metal or larger diameter dies, the end point being when failures no longer occur. The panels are examined at low magnification (5 to 10x) after each bend for fracture of the coating (cracking) and, for loss of adhesion (pickoff), by means of a tape pull off test.

60° Gloss was determined according to ASTM D523-89 a Standard Test Method for Specular Gloss. This test measures the specular (mirror) reflectance from a reference in comparison to a black glass standard. The 60° angle is used for medium gloss specimens and was used for the specimen tests reported in this application.

Adhesion and impact resistance are a Standard Test Method for Measuring Adhesion by Tape Test determined by ASTM D 3359-90 and NCCA Technical Bulletin II-6 a Specification for Evaluation of Film Adhesion by "Cross Hatch" Tape Test After Reverse Impacting respectively. In the ASTM test, a lattice pattern with either six or eleven cuts in each direction is made in the film to the substrate, pressure sensitive tape is applied over the lattice and removed. In the NCCA Technical Bulletin II-6 test, the painted test sample is subjected to reverse impact force by the Gardner Variable Impact Tester using forces up to that required to rupture the substrate of the test specimen. Scotch adhesive tape #610 is applied to the deformed area, air bubbles are

removed by rubbing and the specimen is allowed to set to return to room temperature (but no more than 10 minutes). The tape is removed with a quick pull at right angles to the test surface.

Example 5 - High Solids Non-Aqueous Thinner-Based Dispersion Coating

Table VII

Components	Weight Percent
AMF Resin (PVDF/Acrylic = 80/20)	39.6
Ti-Pure R-960	19.8
Glyceryl tripopionate	19.8
VM & P Naphtha**	19.8
BYK 182 (45% active)*	1.0
Total Weight Solids	59.9

*BYK 182 is a dispersant from BYK-Chemie

**Aliphatic hydrocarbon solvent 119°C to 139°C boiling range

All components were combined, charged into a grinding container with 4 mm glass grinding beads, and the formulation was milled for one hour. The resulting paint was a homogeneous fine dispersion with low viscosity (<1000cPs). A wire wound drawdown applicator was used to apply the paint over chromated aluminum panels. Bake schedules of 550°F for 45 seconds, 450°F for 10 minutes, and 350°F for 20 minutes all produced smooth continuous films with 100% crosshatch adhesion.

In the foregoing examples, the vinylidene fluoride polymer and the acrylic modified

fluoropolymers employed in formulating the paint vehicles employed are identified as follows:

PVDF polymers were all commercially available VDF homopolymers sold by Elf Atochem North America, Inc., under the KYNAR[®] trademark.

5 PVDF 1 was KYNAR 500+
PVDF 2 was KYNAR 500
PVDF 3 was KYNAR 500

AMF polymers were all based on PVDF polymer latices synthesized in accordance with procedures used
10 for commercially available PVDF polymers sold by Elf Atochem North America, Inc., under the KYNAR trademark. The AMF polymers were made as described in the specification. The PVDF type polymer in the seed polymer latices and the acrylic monomers and their
15 relative percentages by weight are as follows:

	<u>AMF</u>	<u>PVDF Seed</u>	<u>Acrylic Monomers</u>	<u>Acrylic Monomer Ratio</u>
	AMF 1	KYNAR 730	M.A./EA	70/30
	AMF 2	KYNAR 500	MMA/EMA/BMA	50/40/10
20	AMF (Ex. 4)	KYNAR Flex 2800	MMA/EA/MAA	65/32/3
	AMF (Ex. 5)	KYNAR 730	MMA/EA	70/30

Acrylate monomer abbreviations:

25 MMA = methyl methacrylate
EA = ethylacrylate
EMA = ethyl methacrylate
BMA = butyl methacrylate
MAA = methacrylic acid

The subject matter which applicants regard as their invention is particularly pointed out and distinctly claimed as follows:

We claim:

1. A paint base for dispersion coating which
5 comprises in an amount of from 10% to 90% by weight of the dry resin content an acrylic modified fluoropolymer resin.

2. A paint base as defined in claim 1 wherein
10 the thinner in said paint base is substantially non-aqueous.

3. A paint base as defined in claim 1 wherein the thinner in said paint base is aqueous based.

4. A paint comprising a pigment mixed with a paint base as defined in claim 1.

15 5. A coating derived by applying a paint as defined in claim 4 to a surface on which a coating is desired and evaporating the thinner of said paint.

6. A coating derived by applying a paint base
20 as defined in claim 1 as a varnish on a surface on which a coating is desired and evaporating the thinner of said paint base.

7. An article of manufacture comprising an article having adhered on at least one surface thereof a coating as defined in claim 5.

25 8. An article of manufacture comprising an article having adhered onto at least one surface thereof a coating as defined in claim 6.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/13734

A. CLASSIFICATION F SUBJECT MATTER

IPC(6) :C08L 27/12; B32B 27/00

US CL :428/421; 524/545, 546, 805

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/421; 524/545, 546, 805

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	US 5,646,201 A (ARAKI et al.) 08 July 1997 (08-07-97), columns 3-6.	1-8
X	US 5,439,980 A (YUTANI et al.) 08 August 1995 (08-08-95), columns 3-6.	1-8

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

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21 OCT 1998

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